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DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER 09/762039

INTERNATIONAL APPLICATION NO. INTERNATIONAL FILING DATE PRIORITY DATE CLAIMED  
PCT/EP 99/06059 August 19, 1999 August 24, 1998

## TITLE OF INVENTION:

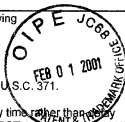
CATIONIC POLYMERS AND THEIR USE

APPLICANT(S) FOR DO/EO/US

Son Nguyen KIM, Axel SANNER, Volker SCHEHLMANN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
  2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
  3. /X/ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Article 29(1) and 39(1).
  4. / / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
    - a. /X/ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b. / / has been transmitted by the International Bureau.
    - c. / / is not required, as the application was filed in the United States Receiving Office (RO/USO).
  6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. / / Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
    - a. / / are transmitted herewith (required only if not transmitted by the International Bureau).
    - b. / / have been transmitted by the International Bureau.
    - c. / / have not been made; however, the time limit for making such amendments has NOT expired.
    - d. / / have not been made and will not be made.
  8. / / A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).
  9. /X/ An oath or declaration of the inventor(s) (35 U.S.C. 171(c)(4)).
  10. / / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
11. /X/ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. /X/ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. /X/ A FIRST preliminary amendment.
  - / / A SECOND or SUBSEQUENT preliminary amendment.
  14. / / A substitute specification.
  15. / / A change of power of attorney and/or address letter.
  16. /X/ Other items or information.  
International Search Report  
International Preliminary Examination Report



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U.S. Appl. No. (If Known) INTERNATIONAL APPL. NO.  
09/762039 PCT/EP99/06059ATTORNEY'S DOCKET NO.  
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	CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO .....	\$860.00	860.00
International preliminary examination fee paid to USPTO (37 CFR 1.482).....	\$690.00	
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....	\$700.00	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....	\$1000.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied pro visions of PCT Article 33(2)-(4).....	\$100.00	

ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 860.00

Surcharge of \$130.00 for furnishing the oath or declaration  
later than / / 20 / / 30 months from the earliest  
claimed priority date (37 CFR 1.492(e)).

Claims	Number Filed	Number Extra	Rate
Total Claims	15 -20		X\$18.
Indep. Claims	1-3		X\$80.
Multiple dependent claim(s) (if applicable)		+270.	
TOTAL OF ABOVE CALCULATION			=
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			

SUBTOTAL = \$860.00

Processing fee of \$130. for furnishing the English  
translation later than / / 20 / / 30 months from the  
earliest claimed priority date (37 CFR 1.492(f)).

TOTAL NATIONAL FEE = \$860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)).

The assignment must be accompanied by an appropriate cover  
sheet (37 CFR 3.28, 3.31) \$40.00 per property = 40.00

TOTAL FEES ENCLOSED = \$ 900.00

Amount to be  
refunded: \$  
Charged \$

- a./X/ A check in the amount of \$900.00 to cover the above fees is enclosed.  
b./I/ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.  
c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.
- NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

Herbert B. Keil  
NAME  
18,967  
Registration No.

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09/762039

JG07 Rec'd PCT/PTO 01 FEB 200

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the U.S. Nationalization Application  
of PCT/EP99/06059 of  
KIM et al.

BOX PCT

Intl. Filing Date: August 19, 1999

US Serial No.: TO BE ASSIGNED

Filed: Herewith

For: CATIONIC POLYMERS AND THEIR USE

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir,

Prior to examination of the above-identified U.S. National Stage application, kindly amend the application as follows.

IN THE CLAIMS

Claim 7, line 1, delete "to 6" to --1--.

Claim 12, line 1, change "one of claims 1 to 6" to --claim 1--.

Claim 13, lines 1 and 2, change "one of claims 1 to 6" to --claim 1--.


REMARKS

The claims have been amended to eliminate multiple dependency and to place them in better form for U.S. practice. Favorable action on the application is solicited.

Please charge any shortage in fees due in connection with the filing of this paper, to Deposit Account No. 11-0345. Please credit any excess fees to such deposit account.

Respectfully submitted,

KEIL & WEINKAUF

  
Herbert B. Keil  
Reg. No. 18,967

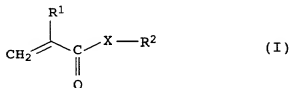
1101 Connecticut Avenue, N.W.  
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(202) 659-0100  
HBK/mks

## Cationic polymers and their use

The present invention relates to cationic polymers obtainable by  
5 free-radical copolymerization of

(a) from 50 to 70% by weight of one or more monomers of the formula I

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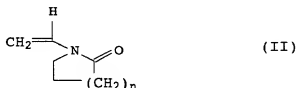


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X = O, NR<sup>1</sup>,  
R<sup>1</sup> = H, C<sub>1</sub>-C<sub>8</sub>-alkyl,  
R<sup>2</sup> = tert-butyl,

20

(b) from 5 to 45% by weight of one or more monomers of the formula II



25

where  $n = 1$  to 3,

30

(c) from 5 to 40% by weight of a monoethylenically unsaturated monomer having at least one amine-containing group,

(d) from 0 to 5% by weight of a polyalkylene oxide-containing silicone derivative.

35 where up to 40% by weight, based on (a), (b), (c) and (d), of the monomer (a) can be replaced by a monomer of the formula I where  $R^2 = C_2-C_{22}$ -alkyl.

In cosmetics, polymers with film-forming properties are used for setting hair, improving its structure and for styling the hair. These hair treatment compositions generally comprise a solution of the film former in an alcohol or a mixture of alcohol and water.

45 Hair-setting compositions are generally sprayed onto the hair in the form of aqueous-alcoholic solutions. After the solvent has evaporated, the hair is held in the desired shape at the mutual

points of contact by the polymer which is left behind. The polymers should on the one hand be sufficiently hydrophilic that they can be washed out of the hair, but on the other hand should be hydrophobic so that the hair treated with the polymers retains

- 5 its shape and does not become sticky, even at high atmospheric humidity. In order to achieve an as efficient a hair-setting action as possible, it is also desirable to use polymers which have a relatively high molecular weight and a relatively high glass transition temperature (at least 15°C).

10

A further requirement of hair treatment compositions is to give the hair a natural appearance and shine, e.g. even when the hair concerned is by its very nature thick and/or dark.

- 15 A disadvantage of many known hair-setting polymers is the "flaking" effect, i.e. a white, dandruff-like residue remains on the hair after combing. This is generally regarded as extremely unpleasant by the users. The "flaking" effect is particularly noticeable in people with dark hair and/or particularly thick
- 20 hair. The possibility of using hair-setting formulations which have this effect is thus significantly impaired particularly in the Asian market. Possible causes of the "flaking" effect are considered to be inter alia the chemical structure of the hair-setting polymers used and, in particular, the particle size
- 25 of the spray.

In addition to the abovementioned properties, hair-setting polymers should therefore preferably have high propellant compatibility in order to permit formulation in spray cans under

30 very high pressure. This applies both to the classical propellant based on propane/butane and also to their replacements, e.g. those based on dimethyl ether.

Cationic hair-setting polymers are known, for example, from

- 35 US 3,914,403 and 3,954,960 and US 4,057,533.

These polymers consist of vinylpyrrolidone, a quaternizable monomer, for example dimethylaminoethyl methacrylate (DMAEMA) and optionally a further monomer.

40

WO 90/01920, WO 96/19966 and WO 96/20694 describe polymers of vinylpyrrolidone, a quaternizable monomer and up to 49% of a further hydrophobic polymer.

- 45 The compatibility of these polymers with the propellant propane/butane is not, however, sufficient for all desired applications. In addition, the products are very sticky as a result of the high

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VP content and under conditions of high atmospheric humidity lose their setting action.

Anionic polymers with propane/butane compatibility are already known, including polymers based on tert-butyl acrylate and tert-butyl methacrylate.

EP-A-379 082 describes, for example, a hair-setting composition comprising, as film former, a copolymer which comprises, in copolymerized form,

- A) from 75 to 99% by weight of tert-butyl (meth)acrylate,
  - B) from 1 to 25% by weight of (meth)acrylic acid and
  - C) from 0 to 10% by weight of a further free-radical
- better propane/butane compatibility, the wash-off is at the same time significantly impaired.

Hair-setting compositions based on this copolymer which comprise only components A) and B) make the hair too hard and have too low a propane/butane compatibility. Copolymers which additionally comprise a monomer C) are in need of improvement as regards their wash-off.

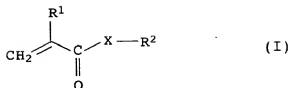
DE-A-43 14 305 describes, like EP-A-379 082, a hair-setting polymer based on tert-butyl (meth)acrylate and (meth)acrylic acid which comprises from 0 to 60% by weight of a C<sub>1</sub>-C<sub>18</sub>-alkyl (meth)acrylate or a mixture thereof with N-C<sub>1</sub>- to C<sub>18</sub>-alkyl (meth)acrylamides in copolymerized form. Although in some cases additional monomers with a carbon number greater than 8 lead to better propane/butane compatibility, the wash-off is at the same time significantly impaired.

It is an object of the present invention to provide novel cosmetic compositions, in particular hair treatment compositions, which, in addition to the good setting properties, have high propellant compatibility and essentially do not exhibit a "flaking" effect. These compositions should preferably make the hair smooth and soft.

Surprisingly, we have found that this object is achieved by cosmetic compositions which comprise at least one water-soluble or water-dispersible cationic polymer which is obtainable by free-radical polymerization of

- (a) from 50 to 70% by weight of one or more monomers of the formula I

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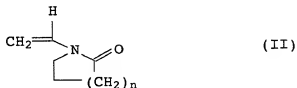
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$\text{X} = \text{O}, \text{NR}^1,$   
 $\text{R}^1 = \text{H}, \text{C}_1\text{-C}_8\text{-alkyl},$   
 $\text{R}^2 = \text{tert-butyl},$

10

- (b) from 5 to 45% by weight of one or more monomers of the formula II

15



where  $n = 1$  to  $3$ ,

20

- (c) from 5 to 40% by weight of a monoethylenically unsaturated monomer having at least one amine-containing group,

- (d) from 0 to 5% by weight of a polyalkylene oxide-containing silicone derivative,

25

where up to 40% by weight, based on (a), (b), (c) and (d), of the monomer (a) can be replaced by a monomer of the formula I where  $\text{R}^2 = \text{C}_2\text{-C}_{22}\text{-alkyl}$ .

30

Preferred monomers (a) are compounds of the formula I in which  $\text{R}^1$  is H and  $\text{CH}_3$ , and X is O and NH; particular preference is given to tert-butyl acrylate, N-tert-butylacrylamide and/or tert-butyl methacrylate.

35

Monomer I can also consist of mixtures having varying meanings of  $\text{R}^1$  and X, preference being given to the monomers (a) where  $\text{X} = \text{NR}^1$  only being used in amounts up to 20% by weight, based on (a), (b) and (c).

40

The monomer (a) is preferably used in amounts of from 51 to 65% by weight, monomer (b) is preferably used in amounts of from 7 to 39% by weight, and monomer (c) is preferably used in amounts of from 10 to 30% by weight.

45

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For the purposes of the present invention, the term "C<sub>2</sub>-C<sub>22</sub>-alkyl" includes straight-chain, branched and cyclic alkyl groups. They are preferably straight-chain alkyl groups and particularly preferably branched alkyl groups.

5

Preferred monomers of the formula I where R<sup>2</sup> = C<sub>2</sub>-C<sub>22</sub>-alkyl are the following compounds:

- n-butyl (meth)acrylate, n-octyl (meth)acrylate, 1,1,3,3-tetramethylbutyl (meth)acrylate, ethylhexyl (meth)acrylate, n-nonyl (meth)acrylate, n-decyl (meth)acrylate, n-undecyl (meth)acrylate, tridecyl (meth)acrylate, myristyl (meth)acrylate, pentadecyl (meth)acrylate, pamityl (meth)acrylate, heptadecyl (meth)acrylate, nonadecyl (meth)acrylate, arrachinyl (meth)acrylate, behenyl (meth)acrylate, 15 lignocerenyl (meth)acrylate, cerotinyl (meth)acrylate, melissinyl (meth)acrylate, palmitoeinyl (meth)acrylate, oleyl (meth)acrylate, linolyl (meth)acrylate, stearyl (meth)acrylate, lauryl (meth)acrylate and mixtures thereof and N-tert-butyl(meth)-acrylamide, N-octyl(meth)acrylamide, 1,1,3,3-tetramethylbutyl- 20 (meth)acrylamide, ethylhexyl(meth)acrylamide, N-nonyl(meth)-acrylamide, N-decyl(meth)acrylamide, N-undecyl(meth)acrylamide, tridecyl(meth)acrylamide, myristyl(meth)acrylamide, pentadecyl(meth)acrylamide, palmityl(meth)acrylamide, heptadecyl(meth)-acrylamide, nonadecyl(meth)acrylamide, arrachinyl(meth)- 25 acrylamide, behenyl(meth)acrylamide, lignocerenyl(meth)-acrylamide, cerotinyl(meth)acrylamide, melissinyl(meth)-acrylamide, palmitoleinyl(meth)acrylamide, oleyl(meth)acrylamide, linolyl(meth)acrylamide, stearyl(meth)acrylamide, lauryl(meth)-acrylamide and mixtures thereof.

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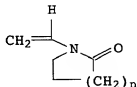
Very particular preference is given to:

n-butyl (meth)acrylate, N-octyl(meth)acrylamide, lauryl (meth)acrylate and stearyl (meth)acrylate, where the term "(meth)acrylate" covers methacrylates and acrylates.

35

Monomers (b) are compounds of the structure II

40



(II)

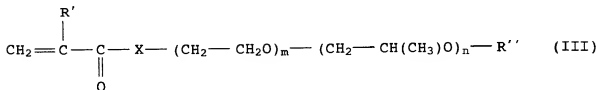
where n = 1 to 3,

- 45 preferably vinylpyrrolidone (VP), vinylcaprolactam (VCap) or mixtures thereof.



Some of (II), up to 4% by weight, based on the total (a) + (b) + (c), can be replaced by a hydrophilic nonionic monomer of the structure III

5



10

R' = H, CH<sub>3</sub>

X = O, NH

m = from 0 to 50

n = from 0 to 50

15

m + n ≥ 5

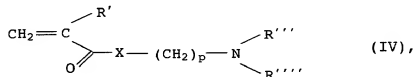
R'' = H, C<sub>1</sub>-C<sub>22</sub>-alkyl or phenyl.

In formula III, R' is preferably a hydrogen atom and a C<sub>1-4</sub>-alkyl group, a methyl group being particularly preferred. Examples of  
 20 such a (meth)acrylate monomer include hydroxy[*lacuna*] (meth)-acrylate, hydroxypropyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol mono(meth)acrylate, ethoxypolyethylene glycol mono(meth)-  
 25 acrylate, butoxypolyethylene glycol mono(meth)acrylate and phenoxypolyethylene glycol mono(meth)acrylate.

Monomers which are used as monomers (c) are those which have at least one mononethylenically unsaturated group and at least one  
 30 amine-containing group.

Preferred monomers (c) are compounds represented by the following structure IV

35



40 where

R' = H, CH<sub>3</sub>

X = O, NH

R'', R''' = are identical or different and can be

45

CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>, tert-C<sub>4</sub>H<sub>9</sub>

p

= 1 to 5

Particularly suitable monomers (c) are:

- N,N-dimethylaminoethyl (meth)acrylate
- N,N-dimethylaminopropyl (meth)acrylate
- N,N-dimethylaminoethyl(meth)acrylamide
- 5        - N,N-dimethylaminopropyl(meth)acrylamide.

Very particularly suitable monomers (c) are:

- N,N-dimethylaminoethyl methacrylate
- N,N-dimethylaminoethylmethacrylamide
- 10        • N,N-dimethylaminopropylmethacrylamide.

The monomers (c) are used in amounts of from 5 to 40% by weight, preferably from 10 to 30% by weight.

- 15 Suitable silicone derivatives (d) are the compounds known under the INCI name dimethicone copolyols or silicone surfactants, such as, for example, those obtainable under the trade names Abil® (T. Goldschmidt), Alkasil® (Rhône-Poulenc), Silicone Polyol Copolymer® (Genesee), Belsil® (Wacker), Silwet® (Witco, Greenwich, CT, USA) or Dow Corning (Dow Corning). These include
- 20 compounds with the CAS numbers 64365-23-7; 68937-54-2; 68938-54-5; 68937-55-3.

The monomers of the groups (a) to (d) can in each case be used

25 individually or in a mixture with other monomers from the same group.

The polymers can be prepared by processes of free-radical initiated polymerization known per se, e.g. by solution

30 polymerization, emulsion polymerization, suspension polymerization, precipitation polymerization, inverse suspension polymerization or inverse emulsion polymerization, without limiting the methods which can be used thereto.

- 35 The polymers are advantageously prepared using solution polymerization in solvents such as water, methanol, ethanol, isopropanol or mixtures of these solvents. The amounts of monomers and solvents are expediently chosen to give from 30 to 70% by weight strength solutions.

40

The polymerization is usually carried out at temperatures of from 50 to 140°C and at atmospheric pressure or under autogeneous pressure.

- 45 Initiators which can be used for the free-radical polymerization are the water-soluble and water-insoluble peroxo and/or azo compounds customary for this purpose, for example alkali metal or

ammonium peroxydisulfates, dibenzoyl peroxide, tert-butyl  
perpivalate, tert-butyl per-2-ethylhexanoate, di-tert-butyl  
peroxide, tert-butyl hydroperoxide, azobisisobutyronitrile,  
azobis(2-amidinopropane) dihydrochloride or 2,2'-azobis(2-methyl-  
5 butyronitrile). Also suitable are initiator mixtures or redox  
initiator systems such as ascorbic acid/iron(II) sulfate/sodium  
peroxodisulfate, tert-butyl hydroperoxide/sodium sulfite,  
tert-butyl hydroperoxide/sodium hydroxymethanesulfinate. The  
initiators can be used in the customary amounts, for example in  
10 amounts of from 0.05 to 5% by weight, based on the amount of  
monomers to be polymerized.

The cosmetic preparations preferably comprise from 0.2 to 20% by  
weight of the polymer.

15 The invention further relates to a process for the preparation of  
the above-described polymers, in which, following the  
polymerization, which is preferably carried out as a solution  
polymerization, the resulting polymer is treated directly with  
20 hydrogen peroxide and/or activated carbon and/or a volatile  
vegetable oil (essential oil) at a temperature between 70 and  
120°C.

Hydrogen peroxide is used here in an amount up to 1% by weight,  
25 activated carbon up to 5% by weight and the essential oil up to  
1% by weight, in each case based on the polymer solution.

Suitable essential oils are, for example, lavender oil, rose oil,  
cinnamon oil, almond oil and coconut oil.

30 This process achieved an improvement in the odor and also the  
color of the polymer.

The polymers in the cosmetic preparations are preferably either  
35 partially or completely neutralized using a monohydric acid or a  
polyhydric acid or a polycarboxylic acid, or are quaternized in a  
customary manner using a quaternizing agent (alkyl halide or  
dialkyl sulfate).

40 In particular, the polymer is partially or completely neutralized  
using phosphoric acid or an acid mixture containing phosphoric  
acid.

Acids which can be used are organic acids, mono-, di-, tricarboxylic acids (e.g. fatty acid, lactic acid, tartaric acid, citric acid) or mineral acids (e.g. hydrochloric acid,  $H_2SO_4$ ,  $H_3PO_4$ ).

5

In order to keep the residual vinyl lactam (VP or VCap) content low, the product solution, following polymerization, is afterpolymerized using 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexane, (Trigonox 101) at about 130°C/3-10 h. This lowers the

10 residual content of vinyl lactam monomers to &lt; 100 ppm.

The invention also relates to the use of the novel polymers for cosmetic preparations, in particular as setting polymers in hair spray, foam setting compositions, hair mousse, hair gel and

15 shampoos.

Other suitable fields of use are cosmetic skin preparations and nail varnishes.

20 The novel polymers preferably have a glass transition temperature above 25°C and a K value of from 25 to 70, preferably from 25 to 50 (measured in accordance with Fikentscher).

The invention further relates to cosmetic hair preparations

25 comprising

(a) from 0.2 to 20% by weight of a polymer as claimed in one of claims 1 to 6,

30 (b) from 0 to 10% by weight of a conventional hair-setting polymer,

(c) from 0 to 1% by weight of a water-dispersible siloxane-containing compound,

35

(d) from 30 to 99.5% by weight of a solvent or solvent mixture of alcohol, in particular ethanol, and water,

40 (e) from 0 to 60% by weight of a propellant of dimethyl ether and/or propane/butane,

(f) from 0 to 0.3% by weight of a cosmetically suitable additive.

45

It is also possible to mix the polymers to be used according to the invention with conventional hair cosmetics polymers if the intention is to achieve particular properties. Examples of conventional hair cosmetics polymers are

5

- cationic (quaternized) polymers, e.g. cationic polyacrylate copolymers based on N-vinyl lactams and derivatives thereof (N-vinylpyrrolidone, N-vinylcaprolactam etc.) and customary cationic hair-conditioning polymers, e.g. Luvisquat® (copolymer of vinylpyrrolidone and vinylimidazolium methochloride), Luvisquat® Hold (copolymer of quaternized N-vinylimidazole, N-vinylpyrrolidone and N-vinylcaprolactam), Merquat® (polymer based on dimethyldiallylammonium chloride), Gafquat® (quaternary polymers produced by reacting polyvinylpyrrolidone with quaternary ammonium compounds), polymer JR (hydroxyethylcellulose containing cationic groups), polyquaternium products (CTFA names), etc.;

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- nonionic, water-soluble or water-dispersible polymers or oligomers, such as polyvinylcaprolactam, e.g. Luviskol Plus (BASF), or polyvinylpyrrolidone and copolymers thereof, in particular with vinyl esters, such as vinyl acetate, e.g. Luviskol VA 37 (BASF); polyamides, e.g. those based on itaconic acid and aliphatic diamines;
- amphoteric or zwitterionic polymers such as the octylacrylamide-methyl methacrylate - tert-butylaminoethyl methacrylate - 2-hydroxypropyl methacrylate copolymers, obtainable under the names Amphomor® (Delft National), and zwitterionic polymers, as disclosed, for example, in German Patent Applications DE 39 29 973, DE 21 50 557, DE 28 17 369 and DE 37 08 451. Acrylamidopropyltrimethylammonium chloride - acrylic acid or - methacrylic acid copolymers and alkali metal and ammonium salts thereof are preferred zwitterionic polymers. Other suitable zwitterionic polymers are methacroylethylbetain - methacrylate copolymers, which are obtainable commercially under the name Amersette® (AMERCHOL);
- nonionic, siloxane-containing, water-soluble or dispersible polymers, e.g. polyethersiloxanes, such as Tegopren® (Goldschmidt) or Belsil® (Wacker).

The polymers to be used according to the invention are generally suitable as hair-setting polymers having a conditioning action in cosmetic preparations, especially in cosmetic hair preparations such as hair treatments, hair lotions, hair rinses, hair emulsions, fluids for treating hair ends, neutralizing agents for

45

permanent waves, "hot-oil treatment" preparations, conditioners, shampoos, setting lotions or hair sprays.

- Depending on the field of use, the cosmetic hair preparations can be applied as a spray, foam, gel, gel spray or mousse. Preference is given to the use as a hair spray.

- As well as containing the novel polymers and suitable solvents such as water or water/alcohol mixtures, the cosmetic hair preparations can also contain additives which are customary in cosmetics, such as emulsifiers, preservatives, perfume oils, care substances such as panthenol, collagen, vitamins, protein hydrolysates, stabilizers, pH regulators, dyes and other customary additives.

- 15 A particularly suitable additive for the polymers according to the invention are fatty acid amides, in particular those with a chain length of  $C_{12}$ - $C_{22}$ . Particular preference is given to erucamide and stearamide. The fatty acid amides are used in an amount of up to 0.1% by weight, based on the polymer.

The polymers according to the invention can also be used in cosmetic preparations for protecting and caring for the skin, for example as moisturizing cream or lotion.

- 25 General preparation procedure (solution polymerization)

#### Example 1

- 30 Feed 1: 1200 g of a monomer mixture of 612 g of tert-butyl acrylate, 120 g of dimethylaminopropylacrylamide and 468 g of vinylpyrrolidone  
Feed 2: 2.4 g of Wako V59 = 2,2'-azobis(2-methylbutyronitrile) in 450 g of ethanol  
35 Feed 3: 3.6 g of Wako V59 in 90 g of ethanol  
Feed 4: 77 g of 40% strength (in ethanol) phosphoric acid

- A mixture of 240 g of Feed 1, 60 g of Feed 2 and 270 g of ethanol was heated to 75°C. After polymerization had started, recognizable from an increase in viscosity, the remainder of Feed 1 was added over 4 h and Feed 2 was added over 5 h at 78°C with stirring, and the mixture was polymerized for a further 4 h at 80°C. After Feed 3 has been metered in over 1/2 h, the product was after-polymerized for 8 h at 80°C. At a temperature of about 40°C, Feed 45 4 was metered in with stirring over about 30 min to give a clear pale yellow solution.

## 12

The other products in the table below can be prepared by a similar method. The polymers have a K value (measured in 1% strength ethanolic solution) of from 37 to about 45 and a propane/butane compatibility of > 60%.

5

The table below gives the values for the composition (% by weight), curl retention, setting, "flaking" and film properties (tack, wash-off and feel).

## 10 Examples

		TBA	TMBA	NtBAM	SMA	DMAPMA	VP	VCap	Curl *) Retention [%]	Set- ting)	Fla- king )	Film *) Tack- wash-off/feel
15	1	51	--	--	--	10	39	--	75	2	2	2 / 2 / 1-2
	2	55	--	--	--	15	30	--	79	1-2	1-2	1-2 / 1-2 / 1-2
	3	40	15	--	--	16	29	--	83	1-2	2	1-2 / 2 / 2
	4	40	--	15	--	16	29	--	87	1-2	2	1-2 / 2 / 1-2
20	5	45	--	--	10	16	29	--	83	1-2	1	2 / 2 / 1
	6	55	--	--	--	17	28	--	87	1-2	1	1-2 / 1-2 / 1
	7	59	--	--	--	23	18	--	71	1-2	1-2	2 / 1 / 1-2
	8	63	--	--	--	30	7	--	76	2	2	2-3 / 1 / 1-2
25	9	60	--	--	--	30	--	10	80	1-2	2	1-2 / 1-2 / 1-2
	10	35	--	--	20	15	30	--	67	2	1-2	2 / 1 / 2
	11	25	--	--	30	15	30	--	60	2-3	1	2-3 / 1 / 1-2
	12	--	--	25	30	15	30	--	77	1-2	1	1-2 / 1 / 2
30	13	--	--	15	35	15	--	30	75	1-2	1-2	1-2 / 1 / 1-2

\*) Curl retention, setting, flaking and film were determined from the VOC 95 aerosol hair spray formulation (containing 50 parts of propane/butane)

	TBA:	tert.-butyl acrylate	VP:	vinylpyrrolidone
35	TMBA:	tert-butyl methacrylate	VCap:	vinylcaprolactam
	NtBAM:	tert-butylacrylamide	DMAPMA:	dimethylaminopropylmethacrylamide
	SMA:	Stearin methacrylate		

- 40 Curl retention is a measure of the hair-setting action under extreme climatic conditions. It is measured in a dummy experiment on hair curls which have been produced using a customary permanent wave on hair about 15 cm in length and sprayed with the spray preparation in question from a distance of 10 cm for 4 sec. After the curls have been hung up in a climatically controlled
- 45 chamber at 25°C and 90% relative atmospheric humidity for a period of 5 h, the relative deformation (extension) of the curls, based on their original shape, is determined. A high value indicates a

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## 13

high setting action, i.e. at 100%, the original shape is completely retained.

The setting test (the setting strength of a polymer on the hair of a dummy head), flaking (residual polymer on the hair after brushing), tack, ability of the polymer to be washed out of the hair and the feel of the treated hair are each assessed on a scale of 1 to 4 by experts:

- 10                    1 = very good  
                       2 = good  
                       3 = still acceptable  
                       4 = poor

## Application examples

15

## • Aerosol hair sprays:

20                    VOC 95    = Polymer No. 1 to 9                    5 parts  
                                          Ethanol    55 parts  
                                          Propane/butane                                   40 parts  
                                          Additive: silicone, perfume

25                    VOC 95    = Polymer No. 1 to 9                    5 parts  
                                          Ethanol    45 parts  
                                          Propane/butane                                   50 parts  
                                          Additive: silicone, perfume

30                    VOC 80    = Polymer No. 1 to 9                    5 parts  
                                          Water    15 parts  
                                          Ethanol    40 parts  
                                          DME     40 parts  
                                          Additive: silicone, perfume

35                    VOC 55    = Polymer No. 1 to 9                    3 parts  
                                          Water    42 parts  
                                          Ethanol    15 parts  
                                          DME     40 parts  
                                          Additive: silicone, perfume

## 40 • Pumpsprays:

                      VOC 95    = Polymer No. 1 to 9                    5 parts  
                                          Ethanol    95 parts  
                                          Additive: silicone, perfume

45                    VOC 80    = Polymer No. 1 to 9                    5 parts  
                                          Water    15 parts

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Ethanol

80 parts

Additive: silicone, perfume

	Polymer 1 to 13 (25% strength aqueous solution)	20.0
5	Cremophor A 25 (Cetareth 25 / BASF)	0.2
	Comperlan KD (Cocamide DEA / Henkel)	0.1
	Water	69.7
	Propane/butane	10.0
	Erucamide	0.0005
10	Other additives: perfume, preservatives ...	

Preparation: Weigh out and dissolve with stirring. Draw off into containers and add propellant.

15	Conditioner Shampoo	[%]
	A) Texapon NSO 28% strength (Sodium Laureth Sulphate / Henkel)	50.0
20	Comperlan KD (Cocamide DEA / Henkel)	1.0
	Polymer 1 to 13 (25% strength aqueous solution)	20.0
	Erucamide	0.001
	q.s. perfume oil	
25	B) Water	27.5
	Sodium chloride	1.5
	q.s. preservative ...	

- Preparation: Weigh out and, with stirring, separately dissolve and mix phases A and B. Slowly stir phase B into phase A.

	Standard O/W cream		
35			
	Oil phase	[%]	CTFA name
	Cremophor A6	3.5	Cetareth-6 (and) Sterayl Alcohol
40	Cremophor A25	3.5	Cetareth-25
	Glycerol monostearate s.e.	2.5	Glyceryl Stearate
	Paraffin oil	7.5	Paraffin Oil
	Cetyl alcohol	2.5	Cetyl Alcohol
45	Luvitol EHO	3.2	Cetearyl Octanoate
	Vitamin E acetate	1.0	Tocopheryl Acetate
	Stearamide	0.001	

15

	Standard O/W cream		
	Nip-Nip	0.1	Methyl- and Propyl-4-hydroxybenzoate (7:3)
5	Water phase	[%]	
	Polymer 1 to 13	1.5	
	Water	73.6	Water
10	1,2-Propylene glycol	1.0	Propylene Glycol
	Germall II	0.1	Imidazolidinyl-Urea

Preparation: Weigh out and, with stirring, separately homogenize the oil phase and the water phase at a temperature of about 80°C. Slowly stir the water phase into the oil phase. Slowly cool to RT with stirring.

	O/W lotion		
20	Oil phase	[%]	CTFA name
	Cremophor A6	2.0	Ceteareth-6 (and) Sterayl Alcohol
25	Cremophor A25	2.0	Ceteareth-25
	Glycerol monostearate	6.0	Glyceryl Stearate
	Paraffin oil	0.9	Paraffin Oil
	Tegiloxan 100	0.1	Dimethicone
30	Cetyl alcohol	1.5	Cetyl Alcohol
	Luvitol EHO	12.0	Cetearyl Octanoate
	Vitamin E acetate	0.4	Tocopheryl Acetate
	Erucamide	0.001	
35	Nip-Nip	0.1	Methyl- and Propyl-4-hydroxybenzoate (7:3)
	Water phase	[%]	
	Polymer 1 to 13	1.0	
40	Water	73.4	Water
	1,2-Propylene glycol	1.0	Propylene Glycol
	Germall II	0.1	Imidazolidinyl-Urea

45

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Preparation: Weigh out and, with stirring, separately homogenize the oil phase and water phase at a temperature of about 80°C. Slowly stir the water phase into the oil phase. Slowly cool to RT with stirring.

5

Example 14 (TBA:DMAPMA:VP:SMA:Belsil = 50.5:15:28:6:0.5)

(1) 2.4 g of Belsil® DMC 6031 (Wacker), 6 g of water and 64 g of ethanol were introduced into the polymerization reactor which had been flushed beforehand with N<sub>2</sub>.

10

(2) The solution was heated to 75°C and stirred.

(3) 242.4 g of TBA, 72 g of DMAPMA, 134.3 g of VP and 28.8 g of SMA were added.

15

(4) 1 g of 2,2'-azobis(2-methylbutyronitrile) (V-59, WAKO), dissolved in 170 g of ethanol, were added.

(5) After a temperature of 70°C had been reached, 96 g of the monomer feed and 17 g of the initiator solution were added.

20

(6) The remaining monomer feed and the initiator addition were added over the course of 4 to 5 hours.

25

(7) After completion of the feed, the mixture was stirred for a further 2 hours at 80°C.

(8) Optionally after treatment with hydrogen peroxide and activated carbon, the polymer was neutralized with lactic acid.

30

The following polymers (Example 15 to 22) were prepared as in Example 14.

35

Table

Example	TBA	DMAPMA	VP	SMA	DMC 6031
15	29	15	25	29	2
16	36	16	28	18	2
17	47	16	28	0	9
18	54	16	28	0	2
19	50	15	28	6	1
20	56	15	28	0	1
21	50	16	28	6	0
22	50.5	15	28	6	0.5

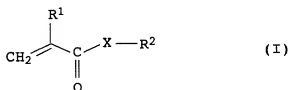
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We claim:

1. A cationic polymer obtainable by free-radical copolymeriza-  
5 tion of

- (a) from 50 to 70% by weight of one or more monomers of the  
formula I

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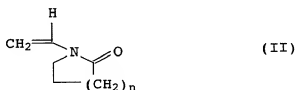
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X = O, NR<sup>1</sup>,  
R<sup>1</sup> = H, C<sub>1</sub>-C<sub>8</sub>-alkyl,  
R<sup>2</sup> = tert-butyl,

20

- (b) from 5 to 45% by weight of one or more monomers of the  
formula II

25



where n = 1 to 3,

30

- (c) from 5 to 40% by weight of a monoethylenically  
unsaturated monomer having at least one amine-containing  
group,

35

- (d) from 0 to 5% by weight of a polyalkylene oxide-containing  
silicone derivative,

where up to 40% by weight, based on (a), (b), (c) and (d), of  
the monomer (a) can be replaced by a monomer of the formula I  
where R<sup>2</sup> = C<sub>2</sub>-C<sub>22</sub>-alkyl.

- 40 2. A polymer as claimed in claim 1, obtainable by free-radical  
copolymerization of

(a) from 51 to 65% by weight of the monomer of the formula I,

45 (b) from 7 to 39% by weight of the monomer of the formula II,

(c) from 10 to 30% by weight of the amine-containing monomer.

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3. A polymer as claimed in claim 1, wherein the monomer (a) is tert-butyl acrylate, N-tert-butylacrylamide and/or tert-butyl methacrylate.
- 5 4. A polymer as claimed in claim 1, wherein the monomer (b) is vinylpyrrolidone and/or vinylcaprolactam.
5. A polymer as claimed in claim 1, wherein the monomer (c) is dimethylaminoalkyl (meth)acrylate and/or dimethylaminoalkyl  
10 (meth)acrylamide.
6. A polymer as claimed in claim 1, wherein the monomers of the formula I where  $R^2 = C_2-C_{22}$ -alkyl are N-butylacrylamide, N-octylacrylamide, lauryl (meth)acrylate or stearyl  
15 (meth)acrylate.
7. The use of polymers as claimed in claim 1 to 6 for cosmetic preparations.
- 20 8. The use as claimed in claim 7 as setting polymers in hair spray, foam setting compositions, hair mousse, hair gel or shampoos.
9. A cosmetic preparation comprising a polymer as claimed in claim 1 in an amount of from 0.1 to 30% by weight, based on the preparation  
25
10. A cosmetic preparation as claimed in claim 9, wherein the polymer is partially or completely neutralized using a monohydric acid, preferably using a polyhydric acid or a polycarboxylic acid, or is quaternized using a quaternizing agent.  
30
11. A cosmetic preparation as claimed in claim 10, wherein the polymer is partially or completely neutralized using phosphoric acid or an acid mixture containing phosphoric acid.  
35
12. The use of polymers as claimed in one of claims 1 to 6 having a glass transition temperature of  $> 25^\circ\text{C}$  and a K value of from 25 to 70, preferably from 35 to 50, for hair cosmetics.  
40
13. A hair cosmetic preparation comprising  
45

19

- (a) from 0.2 to 20% by weight of a polymer as claimed in one of claims 1 to 6,
- 5 (b) from 0 to 10% by weight of a conventional hair-setting polymer,
- (c) from 0 to 1% by weight of a water-dispersible siloxane-containing compound,
- 10 (d) from 30 to 99.5% by weight of a solvent or solvent mixture of alcohol and water,
- (e) from 0 to 60% by weight of a propellant comprising dimethyl ether and/or propane/butane, and
- 15 (f) from 0 to 0.3% by weight of a cosmetically suitable additive.
14. The use as claimed in claim 7 as a constituent in cosmetic
- 20 skin preparations.
15. The use as claimed in claim 14, wherein a fatty acid amide is additionally used.
- 25
- 30
- 35
- 40
- 45

## Cationic polymers and their use

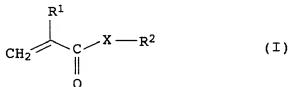
## Abstract

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Cationic polymers are obtainable by free-radical copolymerization of

- (a) from 50 to 70% by weight of one or more monomers of the formula I

10



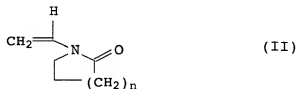
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X = O, NR<sup>1</sup>,  
R<sup>1</sup> = H, C<sub>1</sub>-C<sub>8</sub>-alkyl,  
R<sup>2</sup> = tert-butyl,

20

- (b) from 5 to 45% by weight of one or more monomers of the formula II

25



where n = 1 to 3,

30

- (c) from 5 to 40% by weight of a monoethylenically unsaturated monomer having at least one amine-containing group,
- (d) from 0 to 5% by weight of a polyalkylene oxide-containing silicone derivative,

35

where up to 40% by weight, based on (a), (b), (c) and (d), of the monomer (a) can be replaced by a monomer of the formula I where R<sup>2</sup> = C<sub>2</sub>-C<sub>22</sub>-alkyl.

40

45

# Declaration, Power of Attorney

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We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Cationic polymers and their use

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP 99/06059

August 19, 1999

on \_\_\_\_\_

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

**Application No.**

**Country**

**Day/Month/Year**

**Priority  
Claimed**

19838196.4

Germany

24 August 1998

☒ Yes ☐ No

patentep01 - 25



We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

---

 (Application Number)

---

 (Filing Date)

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 (Application Number)

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 (Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
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<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>

And we (I) hereby appoint Messrs. **HERBERT B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

**Declaration**

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